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Copper(I) Hydroxyapatite Catalyzed Sonogashira Reaction of Alkynes with Styrenyl Bromides. Reaction of *cis*-Styrenyl Bromides Forming Unsymmetric Diynes

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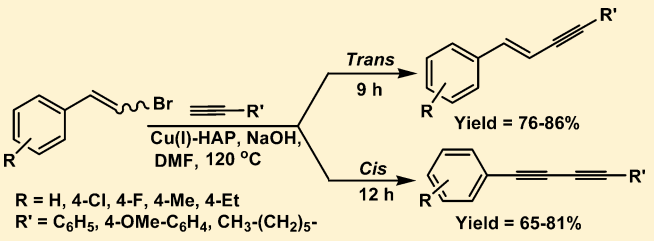
Supporting Information

ABSTRACT: An efficient Sonogashira coupling of terminal alkynes and styrenyl bromides has been achieved under the catalysis of hydroxyapatite-supported copper(I). The *trans*-styrenyl bromides produce the usual *trans*-enyne products, whereas the *cis*-styrenyl bromides lead to unsymmetric 1,3-diynes by the cross coupling of terminal alkyne and the alkyne generated from the *cis*-styrenyl bromide. A series of *trans*-enynes and unsymmetric 1,3-diynes have been synthesized by this protocol.



The conjugated enyne is of great importance because of its presence in many bioactive naturally occurring and synthetic molecules.[1] Moreover, the enynes are valuable synthons, frequently used for the synthesis of polysubstituted benzenes[2] and 1,3-dienes.[3] Thus, several methods have been developed for the synthesis of this scaffold. A widely employed approach is the noble metal-catalyzed dimerization of terminal alkynes.[4] However, the lack of control of regio- and stereoselectivity of the dimerization process is one of its serious limitations. To overcome this problem the metal-catalyzed coupling of an alkyne and a structurally defined organometallic alkene was developed.[5] The difficulty in the preparation of organometallic alkene restricts their uses. A recently developed straightforward approach involving Sonogashira coupling of vinyl halides and terminal alkynes catalyzed by Cu and Pd deserves special mention.[6]

The heterogeneous supported metal catalysts have received considerable current interest because of their operational advantages compared to their homogeneous counterparts.[7] Recently, we demonstrated the application of hydroxyapatite-supported Pd(II) catalyst for coupling of diiodoalkenes and conjugated alkenes[8a] and hydroxyapatite-supported Cu(I)-catalyzed cyanation of styrenyl bromides.[8b] This encouraged us to explore the application of hydroxyapatite-supported Cu(I) catalyst for Sonogashira reaction of terminal alkynes and styrenyl halides with particular interest on coupling of both stereoisomers of styrenyl halides, as in previous reports,[6] only *trans*-vinyl halides have been subjected to the reaction, and we did not find any general Sonogashira reaction with *cis*-vinyl halides except one example where *cis*-styrenyl bromide on reaction with phenyl acetylene catalyzed by CuI in presence of K_3PO_4 produced the corresponding *cis*-1,3-enyne in 27% yield.[6c] We report here our results of Sonogashira coupling of terminal alkynes with *trans*- as well as *cis*-styrenyl bromides catalyzed by hydroxyapatite-supported Cu(I) [Cu (I)-Hap] (Scheme 1). We observed a usual coupling with *trans*-styrenyl bromide to produce *trans*-1,3-enyne product, whereas the corresponding *cis*-counterpart provides unsymmetric 1,3-diyne by the cross coupling of terminal alkyne and the alkyne generated from *cis*-styrenyl bromide.

The diynes are important structural motifs in many natural products and are useful building blocks.[9] Several compounds such as norcapillene,[10] thiarubrine,[11] and falcarindiol[12] containing this subunit showed interesting biological activities. Thus, construction of conjugated diynes, particularly unsymmetric ones, is of considerable interest. Although there are many methods for the synthesis of symmetric diynes,[13] those of unsymmetric diynes are limited. The Cadiot−Chodkiewicz coupling between a haloalkyne and a terminal alkyne under Cu catalysis is the most widely used protocol for the construction of the unsymmetric 1,3-diyne moiety.[14]A few other methods involving coupling of two different alkynes with high loading of one alkyne,[15a] coupling of terminal alkyne and ICH=CHCl,[15b] coupling of terminal bromoalkyne and alkynyl stannane,[15c] and decarboxylative cross-coupling of propiolic acids and terminal alkynes[15d] were also reported. However, there is scope for further improvement with regard to yield, operational simplicity, generality, and cost-efficiency using a novel protocol.

To standardize the reaction conditions, a series of experiments were performed for a representative reaction of *trans*-4-methylstyrenyl bromide and phenylacetylene in the presence of Cu (I)-HAP under different conditions with variation of base, solvent, temperature, and time. It was found that best results were obtained using NaOH in DMF at 120 °C over 9 h (Table

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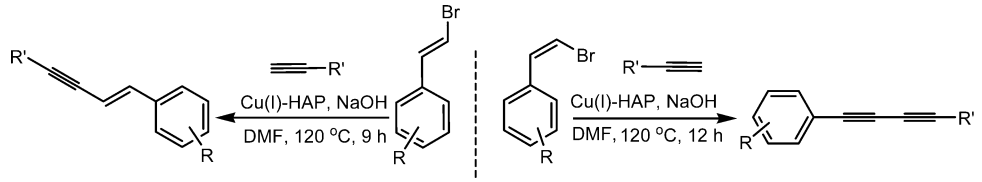
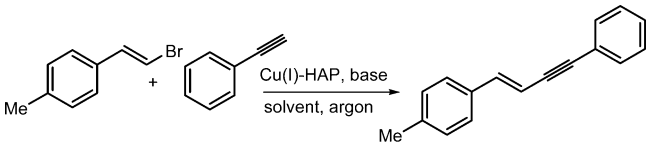
Scheme 1. Sonogashira Coupling of *cis*- and *trans*-Styrenyl Bromides with Terminal Alkynes



1, entry 3). A milder base, K_2CO_3, was also effective (Table 1, entry 1); however, use of NaOH improved the yield.

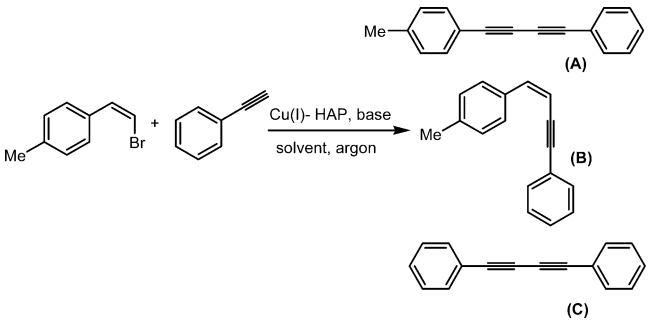
Table 1. Standardization of Reaction Conditions for Coupling of *trans*-Styrenyl Bromide with Acetylene



entry	base	solvent	temp (°C)	time (h)	yield (%)
1	K_2CO_3	DMF	120	7	68
2	NaOH	DMF	120	7	75
3	**NaOH**	**DMF**	**120**	**9**	**82**
4	NaOH	DMF	120	12	82
5	NaOH	THF	75	12	65

Next, to standardize the reaction conditions for *cis*-stryrenyl bromide, we carried out several experiments for a representative reaction of *cis*-4-methylstyrenyl bromide and phenylacetylene in the presence of Cu(I)-HAP with variation of base, solvent, temperature, and time. The use of K_2CO_3 as base in DMF at 120 °C for 9 h produced a mixture of unsymmetric 1,3-diyne (**A**) and *cis*-1,3-enyne (**B**) in a ratio of 55:45 with a chemical yield of 60% (Table 2, entry 1). The change of base from K_2CO_3 to NaOH significantly influenced the product formation

Table 2. Standardization of Reaction Conditions for Coupling of *cis*-Styrenyl Bromide[a] and Acetylene



entry	base	solvent	temp (°C)	time (h)	product ratio (A:B:C)	yield (%)
1	K_2CO_3	DMF	120	9	55:45:0	60
2	NaOH	DMF	120	9	100:0:0	72
3	**NaOH**	**DMF**	**120**	**12**	**100:0:0**	**81**
4	NaOH	DMF	120	15	100:0:0	81
5	NaOH	THF	75	12	100:0:0	62
6[b]	NaOH	DMF	120	12	51:12:37	75

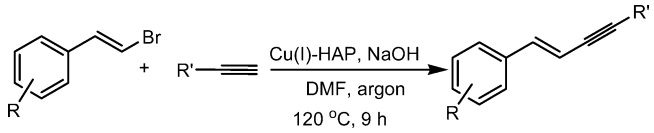
[a]The *cis*-styrenyl bromide was prepared by bromination of the corresponding cinnamic acid followed by base-catalyzed (Et_3N) decarboxylative debromination under microwave irradiation following standard procedures. [b]The reaction was carried out in air.

providing unsymmetric 1,3-diyne (**A**) as sole product when the reaction was carried out in DMF at 120 °C for 12 h under argon (Table 2, entry 3). Interestingly, when the reaction was carried out in air under identical conditions, a mixture of products containing **A**, **B**, and **C** in a 51:12:37 ratio was obtained (Table 2, entry 6). Thus, the reaction conditions as outlined in entry 3, Table 2, were accepted for the reaction of *cis*-styrenyl bromides.

In a typical experimental procedure, a mixture of (*E*)-*β*-bromostyrene or (*Z*)-*β*-bromostyrene, phenylacetylene, NaOH, and Cu (I)-HAP in DMF was heated at 120 °C under argon for a certain period of time as required to complete the reaction (TLC). Standard workup followed by purification by column chromatography provided the product.

Several diversely substituted (*E*)-*β*-bromostyrenes were subjected to reaction with phenylacetylenes and alkyl-substituted alkyne (1-octyne) by this procedure to produce the corresponding 1,3-enynes. The results are summarized in Table 3. The stereochemistry of the double bond was found to be *trans* in all products. The alkyl- and aryl-substituted alkynes react uniformly.

Table 3. Reaction of *trans*-Styrenyl Bromides with Acetylenes



entry	R	R′	yield[a] (%)	ref[b]
1	H	C_6H_5	84	6a
2	4-Cl	C_6H_5	86	6a
3	4-F	C_6H_5	84	6c
4	4-Me	C_6H_5	82	6a
5	4-Et	C_6H_5	80	
6	4-F	4-$OMeC_6H_4$	76	
7	H	$CH_3(CH_2)_5$–	84	17
8	4-Me	$CH_3(CH_2)_5$–	80	

[a]Yields refer to those of purified products characterized by IR and ^1H and ^{13}C NMR spectroscopic data. [b]The known compounds are identified by comparison of their spectroscopic data with those reported.

In a similar procedure, when (*Z*)-*β*-bromostyrenes were reacted with phenylacetylenes, the corresponding unsymmetric 1,3-diynes were obtained. The results are reported in Table 4. Interestingly, we did not isolate the corresponding (Z)-1,3-enyne in any reaction as observed by Mao et al.[6c] The alkyl-substituted alkyne did not undergo this cross-dimerization; instead, only self-dimerization of the alkyne, generated from (*Z*)-bromostyrenes, was isolated (Table 4, entry 7). However, an alkyl-substituted *cis*-vinyl bromide, (Z)-1-bromoundec-1-ene underwent reaction with phenylacetylene successfully (Table 4, entry 8).

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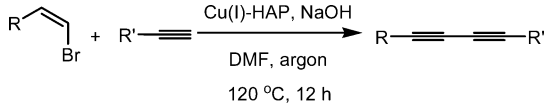
Table 4. Reaction of *cis*-Styrenyl Bromides with Acetylenes



entry	R	R^1	yield[a] (%)	ref[b]
1	C_6H_5–	C_6H_5–	78	15c
2	4-ClC_6H_4–	C_6H_5–	80	18
3	4-FC_6H_4–	C_6H_5–	75	15c
4	4-MeC_6H_4–	C_6H_5–	81	19
5	4-EtC_6H_4–	C_6H_5–	72	
6	4-FC_6H_4–	4-$OMeC_6H_4$–	65	15d
7[c]	C_6H_5-	$CH_3(CH_2)_5$–		
8	$CH_3(CH_2)_8$–	C_6H_5–	65	

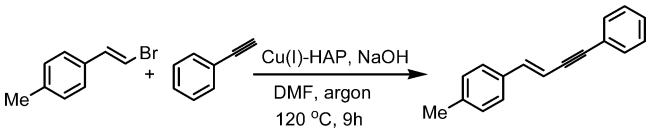
[a]Yields refer to those of purified products characterized by IR and ^1H and ^{13}C NMR spectroscopic data. [b]The known compounds are identified by comparison of their spectroscopic data with those reported. [c]No cross dimer was isolated. Only diphenyldiacetylene, formed by the dimerization of the acetylene generated in situ from styrenyl bromide, was obtained.

Interestingly, we did not observe any self-dimerization of either phenylacetylene or the acetylene generated from (*Z*)-*β*-bromostyrene in the crude reaction products of aryl-substituted alkynes and *cis*-styrenyl bromides. As mentioned previously, when this reaction was carried out in air the mixtures of cross-dimerized and self-dimerized products were obtained. The reason is not very clear to us. This indicates that under argon the cross-dimerization leading to unsymmetric 1,3-diynes is favored over other self-dimerization reactions. In a blank experiment using only (*Z*)-*β*-bromostyrene we isolated a mixture of symmetric 1,3-diynes formed by the self-dimerization of acetylene formed and the *cis*- and *trans*- 1,3-enynes by reaction of *cis*-styrenyl bromide and alkyne formed in situ. This suggests that the reaction of (*Z*)-*β*-bromostyrenes proceed through the intermediacy of alkyne, formed in situ by dehydrohalogenation under basic reaction conditions. Thus, we speculate that Cu(I)-HAP simultaneously interacts with the acetylene generated from (*Z*)-*β*-bromostyrene in situ and phenylacetylene to form a dinuclear Cu(II) acetylide complex X which then produces the unsymmetric 1,3-diyne by single-electron transfer with regeneration of Cu(I)-HAP catalyst, as outlined in Scheme 2. The XPS (X-ray photoelectron spectroscopy) analysis (see the Supporting Information) of the regenerated catalyst shows the oxidation state of copper as Cu(I) supporting this proposition. This type of mechanism in dimerization of acetylenes is not unprecedented.[16]

The reactions are in general very clean and high yielding. The products were obtained pure by simple column chromatography. No ligand or additive was required. The catalyst was recycled for three runs with a gradual decrease in yield of the product (Tables 5 and 6). This might be due to the formation of a coating on the catalyst surface, which possibly reduces its catalytic activity. We also observed considerable leaching of the catalyst (Cu content in the fresh catalyst: 0.3237 mmol/g; Cu content in the recovered catalyst after fourth cycle: 0.2127 mmol/g). This also contributes to the gradual loss of activity.

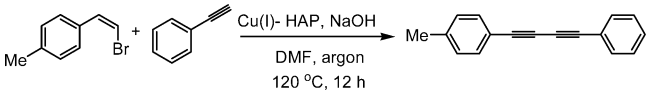
Certainly, our method provides a novel protocol for the synthesis of unsymmetric 1,3-diynes from easily accessible (Z)-*β*-bromostyrenes. Compared to other methods,[14,15] this reaction offers better substrate scope, simplicity in operation without using any ligand and additive, uniformly high yields,[15d]

Table 5. Recyclability Study of Coupling of *trans*-Styrenyl Bromide with Acetylene



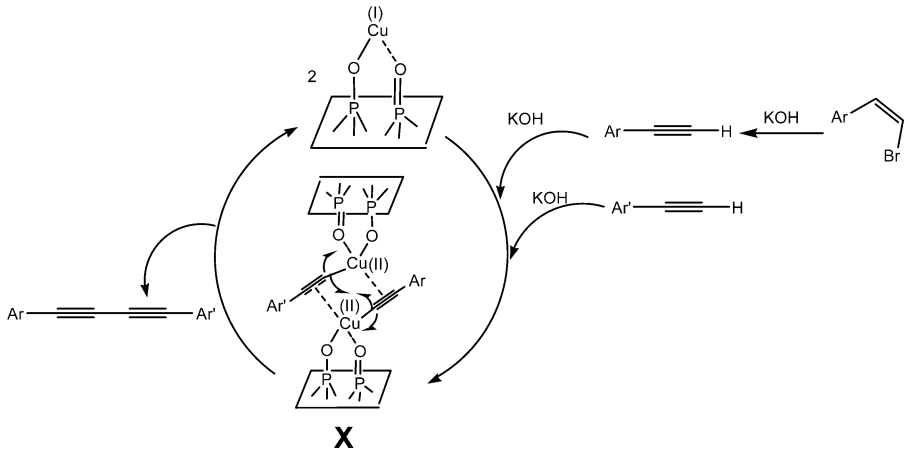
no. of cycles	yield (%)
1	82
2	78
3	70
4	52

Table 6. Recyclability Study of Coupling of *cis*-Styrenyl Bromide with Acetylene



no. of cycles	yield (%)
1	81
2	50
3	27

Scheme 2. Plausible Mechanism for Reaction of *cis*-Styrenyl Bromide with Acetylene



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and cost efficiency involving an inexpensive and recyclable (up to three runs) heterogeneous catalyst.

In conclusion, we have studied the Sonogashira reaction of alkynes with *trans*- and *cis*- styrenyl bromides catalyzed by a heterogeneous hydroxyapatite-supported Cu(I) catalyst. Significantly, although (*E*)-*β*-bromostyrenes provided the usual *trans*-1,3-enynes, the (*Z*)-*β*-bromostyrenes produced the unsymmetric 1,3-diynes by the coupling of alkyne present with the alkyne generated in situ by dehydrohalogenation of *cis*-styrenyl bromide in basic reaction conditions. To the best of our knowledge, we are not aware of any report addressing Sonogashira reaction of alkyne with *cis*-styrenyl halides leading to unsymmetric 1,3-diynes. The other attractive features of this protocol are no use of toxic ligand and additive, easy recovery of the catalyst, generality, and good yields of products. Certainly, this methodology will find useful applications for an easy access to a library of conjugated (*E*)-1,3-enynes and unsymmetric 1,3-diynes.

EXPERIMENTAL SECTION

General Experimental Procedure for Sonogashira Coupling of Alkynes and *β*-Bromostyrenes. Representative Procedure for the Reaction of Phenylacetylene and (*E*)-*β*-Bromostyrene (Table 3, Entry 1). A mixture of (*E*)-*β*-bromostyrene (183 mg, 1 mmol), phenylacetylene (123 mg, 1.2 mmol), NaOH (120 mg, 3 mmol), and Cu(I)-HAP catalyst (100 mg, 3.2 mol %) in DMF (4 mL) was heated with stirring at 120 °C under argon for 9 h (TLC). The reaction mixture was filtered to separate the solid catalyst, which was used for successive cycles. The filtrate was extracted with Et_2O (4 × 15 mL). The extract was washed with water and brine and then dried (Na_2SO_4). Evaporation of the solvent left the crude product which was purified by column chromatography over silica gel (60−120 mesh) (hexane/ether 95: 5) to afford pure (*E*)-1,4-diphenylbut-1-en-3-yne (172 mg, 84%) as a white solid: mp 102−103 °C; IR (KBr) 3002, 2972, 2841, 2192, 1592, 1214, 1020, 981 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.32 (d, J = 15 Hz, 1H), 6.98 (d, J = 15 Hz, 1H), 7.17−7.29 (m, 6H), 7.34−7.42 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 89.0, 91.9, 108.3, 123.5, 126.4 (2C), 128.3, 128.5 (2C), 128.7, 128.9 (2C), 131.6 (2C), 136.5, 141.4. The spectroscopic data (^1H and ^{13}C NMR) are in good agreement with those reported for the authentic sample.[6a] This procedure was followed for all the reactions listed in Table 3.

Representative Procedure for the Reaction of Phenylacetylene and (*Z*)-*β*-Bromostyrene (Table 4, entry 1). The same procedure as in the previous experiment was followed allowing the reaction to go for 12 h (TLC). Extraction and workup provided 1,4-diphenylbuta-1,3-diyne (158 mg, 78%) as a white solid: mp 89−90 °C; IR (KBr) 3049, 2148, 1655, 1638, 1483, 1067, 1024, 915, 755, 685, 524 cm^{-1}, ^1H NMR (500 MHz, $CDCl_3$) δ 7.32−7.39 (m, 6H), 7.53−7.55 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 74.1 (2C), 81.7 (2C), 121.9 (2C), 128.5 (4C), 129.3 (2C), 132.6 (4C). The spectroscopic data (^1H and ^{13}C NMR) are in good agreement with those reported for an authentic sample.[15c]

This procedure was followed for all of the reactions listed in Table 4.

Although these procedures were described with a 1 mmol scale, 10 mmol scale reactions also provided uniform results.

All of these products listed in Tables 3 and 4 were properly characterized. The known compounds were identified by comparison of their spectroscopic data with those reported. The new compounds were characterized by their IR, ^1H NMR, and ^{13}C NMR spectroscopic data and elemental analysis data which are provided below.

1-[(*E*)-4-(4-Ethylphenyl)but-3-en-1-ynyl]benzene (Table 3, entry 5): white solid; mp 81−82 °C; IR (KBr) 3030, 2980, 2890, 2190, 1601, 1505, 1212, 1022, 985 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.29 (t, J = 7.5 Hz, 3H), 2.70 (q, J = 7.5 Hz, 2H), 6.40 (d, J = 16.5 Hz, 1H), 7.10 (d, J = 16.5 Hz, 1H), 7.22 (d, J = 8 Hz, 2H), 7.34−7.40 (m, 5H), 7.53 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.5, 65.4, 89.3, 91.5, 107.2, 123.7, 126.4 (2C), 128.3, 128.4, 128.5 (2C), 131.6 (2C), 133.9, 141.4 (2C), 145.1. Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.13; H, 6.87.

1-Fluoro-4-[(*E*)-4-(4-methoxyphenyl)but-1-en-3-ynyl]-benzene (Table 3, entry 6): white solid; mp 114−115 °C; IR (KBr) 3003, 2975, 2936, 2841, 2138, 1599, 1504, 1436, 1256, 1108, 985 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.32 (d, J = 16 Hz, 1H), 6.90 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 16 Hz, 1H), 7.06 (t, J = 8.5 HZ, 3H), 7.39−7.42 (m, 3H), 7.45 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 87.5, 91.9, 108.3, 114.2 (2C), 115.7 (2C), 127.9 (2C), 133.1 (2C), 134.2, 139.2, 159.7, 161.9, 163.9. Anal. Calcd for $C_{17}H_{13}FO$: C, 80.93; H, 5.19. Found: C, 80.84; H, 5.23.

1-[(*E*)-Dec-1-en-3-ynyl]-4-methylbenzene (Table 3, entry 8): colorless liquid; IR (neat) 2928, 2857, 1448, 951, 746, 684 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 6.5 Hz, 3H), 1.27 −1.36 (m, 4H), 1.41−1.47 (m, 2H), 1.55−1.60 (m, 2H), 2.35−2.39 (m, 5H), 6.12 (d, J = 16.5 Hz, 1H), 6.86 (d, J = 16.5 Hz, 1H), 7.13 (d, J = 8 Hz, 2H), 7.27 (d, J = 8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 19.8, 21.4, 22.7, 28.8, 28.9, 31.5, 80.0, 92.8, 107.9, 126.1 (2C), 129.5 (2C), 134.0, 138.3, 140.0. Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.25; H, 9.75.

1-[4-(4-Ethylphenyl)buta-1,3-diynyl]benzene (Table 4, entry 5): white solid; mp 80−81 °C; IR (KBr) 3049, 2970, 2145, 1655, 1483, 1431, 1256, 1067, 915 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.15 (t, J = 7.5 Hz, 3H), 2.57 (q, J = 7.5 Hz, 2H), 7.08 (d, J = 8 Hz, 2H), 7.23−7.28 (m, 3H), 7.35−7.37 (m, 2H), 7.43−7.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.3, 29.0, 73.4, 74.1, 81.4, 81.8, 119.1, 122.0, 128.1 (2C), 128.5 (2C), 129.3, 132.6 (4C), 146.4. Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.76; H, 6.24.

1-(Trideca-1,3-diynyl)benzene (Table 4, entry 8): colorless viscous liquid; IR (neat) 3311, 2926, 2854, 2245, 1491, 1458, 1215, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 5.4 Hz, 3H), 1.25−1.43 (m, 12H), 1.52−1.62 (m, 2H), 2.35 (t, J = 7 Hz, 2H), 7.26−7.33 (m, 3H), 7.45−7.48 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 19.6, 22.6, 28.7, 28.8, 29.1, 29.2, 29.4, 31.8, 65.1, 74.4, 74.7, 84.9, 122.3, 128.3 (2C), 128.7, 132.5 (2C). Anal. Calcd for $C_{19}H_{24}$: C, 90.42; H, 9.58. Found: C, 90.60; H, 9.40.

ASSOCIATED CONTENT

Supporting Information

Copies of XPS spectra of the fresh and regenerated Cu(I)-HAP; ^1H NMR and ^{13}C NMR spectra of all products listed in Tables 3 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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